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# Study on preparation and property of phenolic-$SiO_2$ core-shell composite hollow microspheres

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**Abstract**

The great advantage of hollow $SiO_2$ microspheres is low density and high-temperature resistance, however, the toughness and wear-resisting property is poor, so it can't be used in the condition of mechanical friction and high-speed shearing. Therefore, phenolic-$SiO_2$ core-shell composite hollow microspheres were prepared by spray coating process, and the properties were measured. The results indicate that the core-shell composite hollow microspheres not only have low density and high-temperature resistance, but also have good toughness and wear-resisting property. The compressive strength was 50 MPa. The density was 0.54-0.65 g/cm$^3$. Temperature resistance was 120℃. Grain diameter was 2～300μm and the percentage of damage on the condition of grinding for 16h was very low. Phenolic-$SiO_2$ core-shell composite hollow microspheres have good prospect in the field of the development of oil gas and spaceflight.



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***Keywords:***phenolic resin; $SiO_2$; composite hollow microsphere; preparation; wear-resisting property

Hollow $SiO_2$ microspheres is a kind of lightweight and non-metallic materials, as it has low density, low thermal conductivity, small dielectric constant, high mechanical strength and perfect heat resistance performance, therefore, hollow microsphere of $SiO_2$ can be used as reduce additive of drilling fluid density[1], wear-resistant and thermal-resistant material, and senior insulating material in some civil and military fields[2].

Due to the hollow $SiO_2$ microsphere is a kind of rigid and hard brittle powder material, so the toughness and wear-resisting property of hollow $SiO_2$ microspheres are poor. Hollow microsphere $SiO_2$ is easy to be cracked as it is used as a reducing agent of drilling fluid density even the a bit shearing, and the service life of hollow $SiO_2$ microspheres is short as it is used as wear resistant material in spaceflight field, which limit greatly its applications in those areas. In order to improve further the

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toughness and wear-resisting property of the hollow $SiO_2$ microsphere, based on the advantages of organic material and inorganic material, organic - inorganic compound hollow microsphere was designed[3] in this article. A kind of phenolic aldehyde-$SiO_2$ core-shell composite hollow microsphere was prepared by spray coating process, and the optimal process parameters of preparation was researched, and the toughness and wear-resisting properties of core-shell composite hollow microsphere were measured through the shearing test and compressive strength test. This study can be useful to explore the application prospect of phenolic aldehyde-$SiO_2$ core-shell composite hollow microsphere in those above-mentioned fields. At the same time, this study can also supply some beneficial technical reference for the design and development of other composite hollow microsphere.

## 1 The design of phenolic -$SiO_2$ core-shell composite hollow microsphere

Some studies display that hollow $SiO_2$ microspheres have the advantages of low density and high-temperature resistance, but the toughness and wear-resisting property of them are poor. However, compared with $SiO_2$, phenolic resin microspheres have characters of low strength, high toughness and perfect wear-resisting property. Therefore, we design a kind of core-shell composite hollow microspheres with hollow microsphere of $SiO_2$ as the core and phenolic resin as the shell. This design develops fully the advantages of two kinds of materials[4, 5]. Hollow $SiO_2$ microspheres as the core can ensure the high strength of the composite microspheres and phenolic resin as the external shell can significantly improve the toughness and wear-resisting performance of the composite microspheres, which makes the original performance be greatly improved, make its application areas and application fields be further enlarged and expanded[6].

## 2 The preparation of phenolic -$SiO_2$ core-shell composite hollow microsphere

Based on the design of phenolic - $SiO_2$ core-shell composite hollow microsphere, utilizing the thermosetting phenolic resin, phenolic -$SiO_2$ core-shell composite hollow microsphere was prepared by the method of spray coating process, the device diagram of spray coating was shown in Fig. 1.

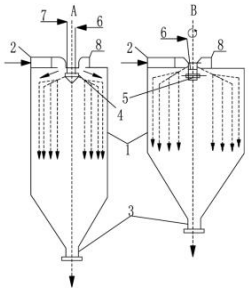



Fig. 1 The internal flow diagram of spray coating device

1 - Autoclave body，2 - Hot gas entrance，3 - Discharging entrance, 4 - Air sprayer, 5 - Centrifugal disc atomizer, 6 - Slurry entrance, 7 - Jet gas entrance, 8 - Regulator of hot gas

### *2.1 Basic principles of surface coating*

Phenolic resin is a kind of organic polymer material and hollow $SiO_2$ microsphere is inorganic material, so it is the most important technical problems to how to realize effective combination between these phenolic resin and hollow $SiO_2$ microspheres during the process of the design and preparation. The final performance of this kind of core-shell composite hollow microsphere was related directly on the surface coated effect and bonding status of organic shell and inner core. To gain a good interface bonding, the following factors must be considered:

(1) to meet thermodynamics of capacitive between the different phase states;
(2) to meet with the co-existence of thermodynamics between the different phase states;
(3) to have good wettabilities between the shell layer and the core.

*2.2 The shell choice of phenolic resin*

Phenolic resin has the advantages of perfect toughness, excellent thermal stability, strong corrosion resistance, good mechanical strength, simple preparation technology and lower prices. Therefore, through using this kind of organic polymer materials as a coating layer of $SiO_2$ hollow microsphere, the toughness and wear-resisting property of the core-shell composite hollow microspheres can be greatly improved. However, phenolic resin which can meet the design of composite hollow microspheres and preparation requirements should have the following characteristics:

(1) must be thermosetting phenolic resin, and can be quickly curing at high temperature condition of spray device;

(2) should be water soluble phenolic resin, which is beneficial to combine effectively between phenolic resin and hollow microsphere of $SiO_2$ surface;

(3) should have good temperature resistance and strong toughness.

According to the above technical requirements, the author has carried out by a large number of experiments and analyzed the feasibility of magnesium phenolic resin, nylon phenol, ammonia phenolic and water-soluble phenolic resin[7] as the polymer shell. Finally we selected water-soluble phenolic resin as the shell material of core-shell composite hollow microsphere.

*2.3 Surface coating technology*

Hollow $SiO_2$ microspheres have been prepared by the plasma sintering technology in our laboratory, whose compressive strength was 50 MPa and whose diameter $d_{50}$ was 46 microns. The SEM diagram as shown in figure 1. We toke these hollow $SiO_2$ microspheres as the core of core-shell composite hollow microspheres. According to plenty of experiments, the optimal concentration of water-soluble phenolic resin and suitable curing temperature were gained. On the basis of the above research, the technology of preparing phenolic-$SiO_2$ core-shell composite hollow microsphere was studied, and the specific process steps were as follows:

(1) to put water soluble phenolic resin to the mixing vessel, add the right amount of water, start the mixing evenly, and make the water-soluble phenolic completely dispersed, keep the viscosity of phenolic resin solution in a reasonable range;

(2) to add the appropriate quantitive hollow $SiO_2$ microspheres and dispersant, keep $SiO_2$ evenly disperse in phenolic solution;

(3) to start the spray coating equipment, set reasonable parameters outlet (into) temperature and carrying gas flow rate and the parameters of cyclone separation, make constant and uniform temperature of equipment, air flow smoothly;

(4) to start the charge pump in reasonable emissions, the slurry suspension was evenly sprayed in the working chamber, water soluble phenolic resin was evenly coated on the surface of hollow microsphere of $SiO_2$, and the solvent was quickly volatilized;

(5) to be sure that phenolic -$SiO_2$ core-shell composite hollow microspheres were automatically assigned in several collection bags under the induced air;

(6) to collect samples of several collection bags for different density range of phenolic - $SiO_2$ core-shell composite hollow microspheres.

## 3 Performance evaluation of core-shell composite hollow microsphere

*3.1 Basic performance*

The true density, morphology and particle size of two kinds of phenolic - $SiO_2$ core-shell composite hollow microspheres were evaluated by SEM scanning. *The particle size distribution of the specimens were determined by a laser particle size analyzer (Beckman Coulter, LS 13 320).* The experimental results were shown in figure 2 - figure 5 and table 1.

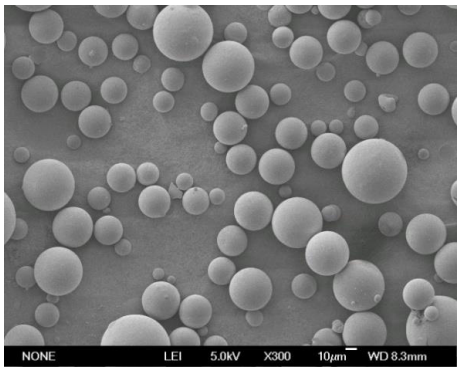



Fig. 2 SEM of hollow microsphere of $SiO_2$

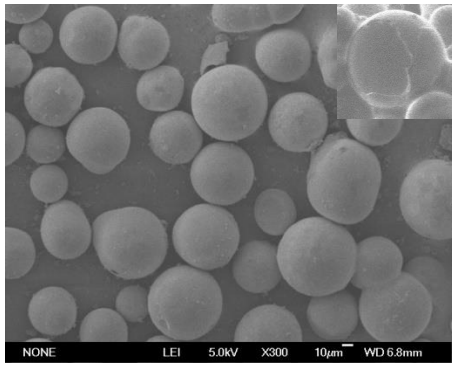
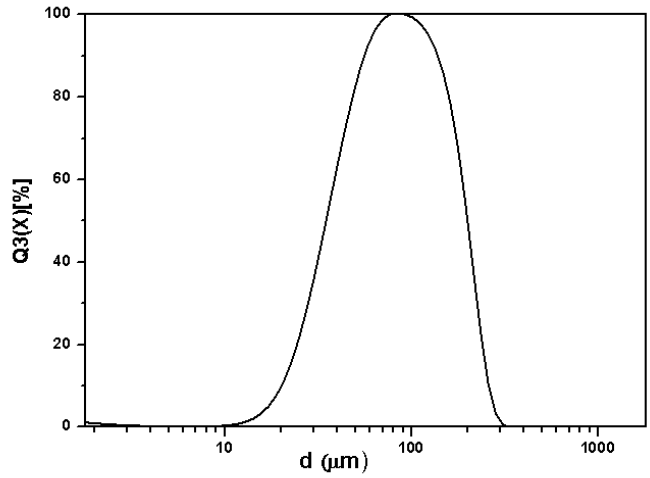
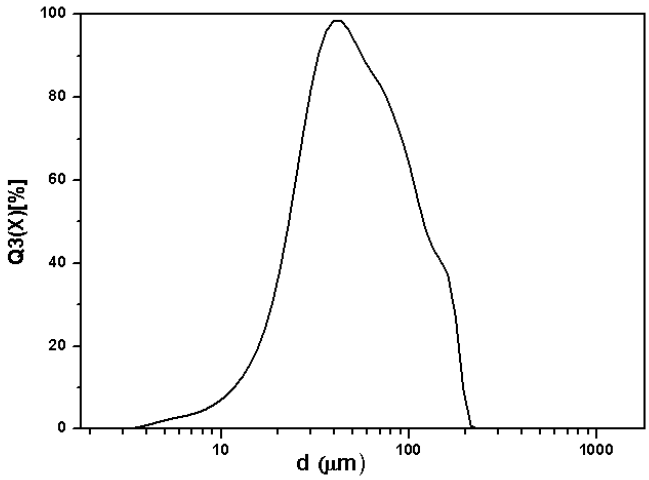



Fig.3 SEM of core-shell composite hollow microsphere




No. 1




No. 2

Fig. 4 particle size distribution of core-shell composite hollow microsphere

Table 1 Density and particle size of core-shell composite hollow microspheres

| No. of composite hollow microsphere | Density (g/cm$^3$) | Particle size ($d_{50}$/μm) |
|---|---|---|
| 1 | 0.54 | 80.0 |
| 2 | 0.65 | 59.6 |

The results of experiments display that the phenolic-$SiO_2$ core-shell composite hollow microspheres have good degree of sphericity, true density is in the range of 0.54 ~ 0.65 g/cm$^3$, and particle size is in the range of 2 ~ 300 um.

*3.2 The performance of wear-resisting*

In order to analyze the wear-resisting property of phenolic - $SiO_2$ core-shell composite hollow microsphere, the method used in drilling fluid density reducing agent to evaluate wear-resisting property was consulted, the steps of this method are as follows:

(1) to prepare 0.2% xanthan glue solution, and be fully hydrated for 24 h;

(2) to put 300 ml xanthan glue solution to high-speed mixer, open mixer, keep mixing speed 5000 RPM, add 30g phenolic-$SiO_2$ core-shell composite hollow microsphere, stirring for 20 min, and make them completely disperse;

(3) to test the density of the slurry by the method of volume weight determination, and the result is recorded as $\rho_1$;

(4) After testing, to adjust mixing speed to 12000 RPM, continuously mix for 1 h, test the density again, and the result is recorded as $\rho_2$;

(5) After testing, to transfer the slurry to a 500 ml airtight aging kettle, and put ten φ17.7 mm steel ball to simulate phenolic-$SiO_2$ core-shell composite hollow microspheres be crashed and fricted. The rotate and age kettle time is 16 h under 120℃;

(6) After the slurry being cooled, to determinate its density and the result is recorded as $\rho_3$;

(7) to compare $\rho_1$、$\rho_2$ and $\rho_3$, and evaluate the property of wear-resisting.

The results were shown in Tab. 2.

Tab. 2 Result on the wear-resisting property of core-shell composite hollow microsphere

| No. composite hollow microsphere | Density(g/cm$^3$) | $\rho_1$(g/cm$^3$) | $\rho_2$ (g/cm$^3$) | $\rho_3$ (g/cm$^3$) |
|---|---|---|---|---|
| hollow glass microsphere | 0.70 | 0.97 | 0.99 | 1.02 |
| 1 | 0.54 | 0.93 | 0.93 | 0.94 |
| 2 | 0.65 | 0.96 | 0.96 | 0.97 |

The results of experiments show that both the hollow glass microsphere and phenolic-$SiO_2$ core-shell composite hollow microspheres have good effect in reducing density, but the density of slurry confected by hollow glass microspheres is significantly increasing after the slurry is stirred in high speed cutting and mechanical collision simulation, which indicates that the wear-resisting performance is poorer. As for the density of slurry confected by phenolic-$SiO_2$ core-shell composite hollow microspheres is almost no change in high speed cutting and mechanical collision simulation, which shows phenolic-$SiO_2$ core-shell composite hollow microspheres have good wear-resisting performance, and can meet the performance requirements of density reducing agent used in drilling fluid.

*3.3 The performance of compressive strength*

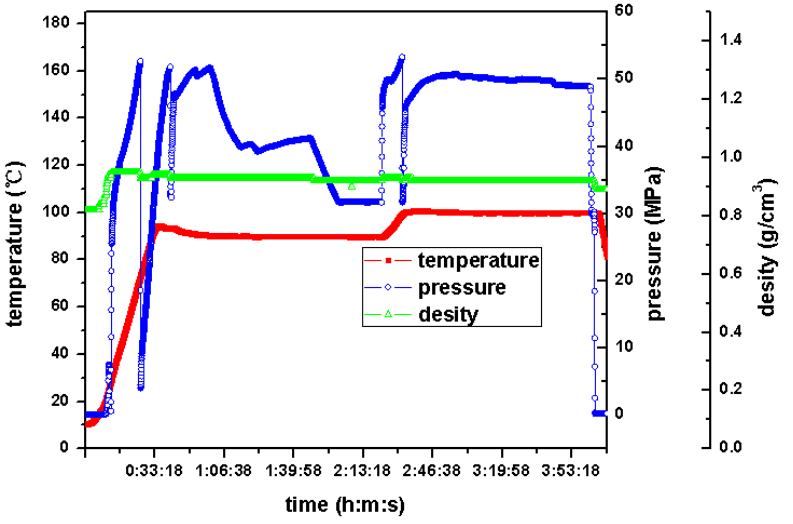
In order to analyze the compressive strength of phenolic-$SiO_2$ core-shell composite hollow microsphere, the results was measured by the compressive strength evaluation device used in cementing industry, the steps of this method are as follows:

(1) to prepare 0.2% xanthan glue solution, and be fully hydrated for 24 h;

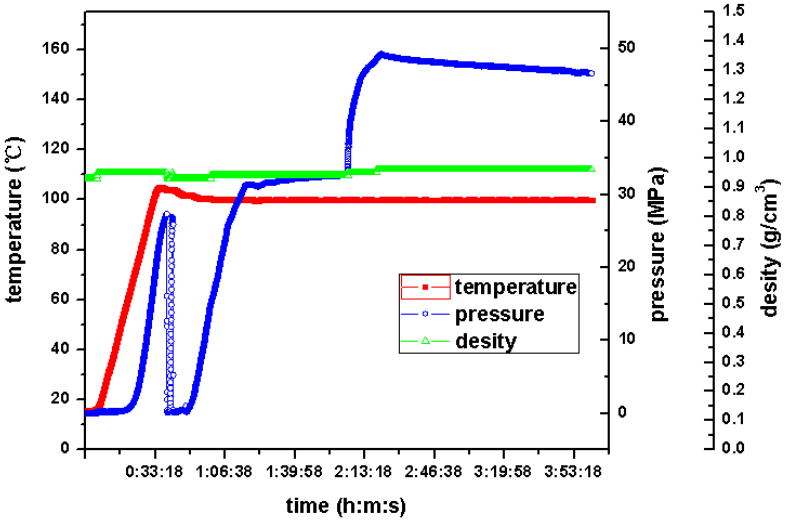
(2) to put 300 ml xanthan glue solution to high-speed mixer, open mixer, keep mixing speed 5000 RPM, add 30g phenolic-$SiO_2$ core-shell composite hollow microsphere, stirring for 20 min, and make them completely disperse;

(3) to put the slurry into the evaluation device of compressive strength, set the testing temperature at 120℃ and the test pressure at 50 Mpa. The device will automatically record the change of the density of slurry;

(4) the results of compressive strength for composite microspheres No.1 and No.2 are shown in Fig. 5.




No.1




No.2

Fig.5 The results of compressive strength for composite microspheres No.1 and No.2

From Fig.5, we can see that the densities of the slurry confected by No.1 and No.2 phenolic - $SiO_2$ core-shell composite hollow microsphere are stable and almost no change, under the experimental conditions of 120 ℃ 50 Mpa, which these core-shell composite hollow microspheres have good compressive strength, and can meet the performance requirements of density reducing agent used in oil & gas fields, aerospace and other fields.

## 4. Conclusion

(1) In view of shortages of hollow microspheres of $SiO_2$ in toughness and shear-resistance property, by comprehensive utilizing the advantages of organic material and inorganic material, phenolic - $SiO_2$ core-shell composite hollow microsphere is designed, and the method to prepare this kind of novel microsphere is determined by spray coating technical method;

(2) Water soluble phenolic resin has good temperature resistance, strong toughness, easy to interface bonding with hollow microspheres of $SiO_2$, so it is suitable as appropriate shell materials to prepare core-shell composite hollow microsphere by spray coating process;

(3) The phenolic-$SiO_2$ core-shell composite hollow microspheres prepared by spray coating process have good degree of sphericity, true density is in the range of 0.54 ~ 0.65 g/cm$^3$, and particle size is in the range of 2 ~ 300 um.

(4) The phenolic-$SiO_2$ core-shell composite hollow microspheres under the condition of high speed stirring and longtime mechanical collision, have a very low breakage rate, which show good wear-resisting performance, and can meet the performance requirements of density reducing agent used in drilling fluid;

(5) The compressive strength of phenol-$SiO_2$ core-shell composite hollow microsphere prepared in this article is more than 50 Mpa, these composite hollow microsphere can meet the performance requirements of density reducing agent used in oil & gas fields, aerospace and other fields, and has good prospect in the above-mentioned fields.

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